METHODS AND APPARATUS FOR CLEANING AND/OR TREATING A SUBSTRATE USING CO_2

Field of the Invention

The present invention relates to methods and apparatus for cleaning and/or treating substrates and, more particularly, to methods and apparatus for cleaning and/or treating substrates using CO_2.

Background of the Invention

Integrated circuits (ICs), optoelectronic devices, micromechanical devices and other precision fabrications are commonly formed using thin films applied to substrates. As part of the fabrication process, it is often necessary to remove or clean a portion or all of the thin film from the substrate. For example, in the manufacture of semiconductor wafers including ICs, a thin photoresist layer may be applied to the semiconductor substrate and subsequently removed.

Contaminants removed from surface features of microelectronic substrates after various manufacturing steps (*e.g.*, after post-ion implant, 'back end of the line' (BEOL) cleans, 'front end of the line' (FEOL) cleans, and post chemical mechanical planarization (CMP) steps) vary in nature and composition dramatically. Accordingly, cleaning and treating steps must address these contaminants with the appropriate chemistries and solvents to either react with, ionize, dissolve, swell, disperse, emulsify, or vaporize them from the substrate. As such, a variety of water and solvent-based systems, and dry cleaning processes have been developed to address the broad variety of waste materials.

Summary of the Invention

According to method embodiments of the present invention, a method for cleaning a microelectronic substrate includes placing the substrate in a pressure chamber. A process fluid including dense phase CO_2 is circulated through the

chamber such that the process fluid contacts the substrate. The phase of the CO_2 is cyclically modulated during at least a portion of the step of circulating the process fluid.

According to further method embodiments of the present invention, a method for cleaning a microelectronic substrate includes placing the substrate in a pressure chamber. A process fluid including dense phase CO_2 is sprayed onto the substrate in a chamber. The phase of the CO_2 is cyclically modulated during at least a portion of the step of spraying the process fluid.

According to further method embodiments of the present invention, a method for cleaning a microelectronic substrate includes providing the substrate in a pressure chamber containing a process fluid including dense phase CO_2 such that the substrate is exposed to the CO_2. The phase of the CO_2 is cyclically modulated by alternating CO_2 mass flow between a supply of CO_2 and the chamber and between the chamber and a low pressure source. The supply of CO_2 is at a higher pressure than the chamber and the low pressure source is at a lower pressure than the chamber.

According to further method embodiments of the present invention, a method for cleaning a microelectronic substrate includes placing the substrate in a pressure chamber. A process fluid including dense phase CO_2 is introduced into the chamber such that the process fluid contacts the substrate to thereby clean the substrate. A portion of the process fluid is removed from the chamber. The portion of the process fluid is re-introduced into the chamber.

According to further method embodiments of the present invention, a method for cleaning a microelectronic substrate includes placing the substrate in a pressure chamber. A process fluid including dense phase CO_2 is introduced into the chamber such that the process fluid contacts the substrate to thereby clean the substrate. A portion of the process fluid is removed from the chamber. The portion of the process fluid removed from the chamber is distilled to separate CO_2 from other components of the process fluid. The separated CO_2 is re-introduced into the chamber.

According to further method embodiments of the present invention, a method for cleaning a microelectronic substrate includes cleaning a substrate in a process chamber using a process fluid including CO_2. The used process fluid is

removed from the process chamber. CO_2 is separated from the used process fluid. The separated CO_2 is reused in the process chamber or a further process chamber.

According to embodiments of the present invention, an apparatus for cleaning a microelectronic substrate includes a pressure chamber and means for circulating a process fluid including dense phase CO_2 through the chamber such that the process fluid contacts the substrate. The apparatus further includes means for modulating the phase of the CO_2 while the process fluid is being circulated.

According to further embodiments of the present invention, an apparatus for cleaning a microelectronic substrate using a process fluid including dense phase CO_2 includes a pressure chamber. A spray member is operative to spray the process fluid onto the substrate in the chamber. The apparatus further includes means for cyclically modulating the phase of the CO_2.

According to embodiments of the present invention, an apparatus for cleaning a microelectronic substrate includes a pressure chamber containing a process fluid including dense phase CO_2. A supply of CO_2 is fluidly connectable to the chamber. The supply of CO_2 is at a higher pressure than the chamber. A low pressure source is fluidly connectable to the chamber. The low pressure source is at a lower pressure than the chamber. Fluid control devices are operable to cyclically modulate the phase of the CO_2 in the chamber by alternating CO_2 mass flow between the supply of CO_2 and the chamber and between the chamber and the low pressure source.

According to embodiments of the present invention, an apparatus for cleaning a microelectronic substrate includes a pressure chamber and a supply of a process fluid including dense phase CO_2 fluidly connected to the chamber. A distilling system includes a still fluidly connected to the chamber and operative to separate CO_2 from the process fluid. The distilling system is operative to re-introduce the separated CO_2 into the chamber or a further chamber.

According to embodiments of the present invention, an apparatus for cleaning a microelectronic substrate includes a process chamber containing a process fluid including CO_2 and means for removing used process fluid from the process chamber. The apparatus further includes means for separating CO_2 from the used process fluid and means for returning the separated CO_2 to the process chamber or a further process chamber for subsequent use.

According to embodiments of the present invention, a process chamber assembly for use with a substrate includes a vessel and a substrate holder. The vessel defines a chamber. The substrate holder has a rotational axis and includes front and rear opposed surfaces. The front surface is adapted to support the substrate. At least one impeller vane extends rearwardly from the rear surface and radially with respect to the rotational axis. The impeller vane is operative to generate a pressure differential tending to hold the substrate to the substrate holder when the substrate holder is rotated about the rotational axis. Preferably, the process chamber assembly includes a plurality of the impeller vanes extending rearwardly from the rear surface and radially with respect to the rotational axis.

According to further embodiments of the present invention, a substrate holder for use with a substrate has a rotational axis and further includes front and rear opposed surfaces. The front surface is adapted to support the substrate. At least one impeller vane extends rearwardly from the rear surface and radially with respect to the rotational axis. The impeller vane is operative to generate a pressure differential tending to hold the substrate to the substrate holder when the substrate holder is rotated about the rotational axis. Preferably, the substrate holder includes a plurality of the impeller vanes extending rearwardly from the rear surface and radially with respect to the rotational axis.

According to method embodiments of the present invention, a method for rotating a substrate holder about a rotational axis includes providing a substrate holder. The substrate holder includes front and rear opposed surfaces. The front surface is adapted to support the substrate. At least one impeller vane extends rearwardly from the rear surface and radially with respect to the rotational axis. The substrate holder is rotated about the rotational axis such that the impeller vane generates a pressure differential tending to hold the substrate to the substrate holder.

According to embodiments of the present invention, a pressure chamber assembly for use with a substrate includes a vessel and a substrate holder assembly. The vessel defines a pressure chamber. The substrate holder assembly includes a substrate holder disposed in the pressure chamber, the substrate holder including a front surface adapted to support the substrate, and a housing defining a secondary chamber. At least one connecting passage provides fluid

communication between the front surface of the substrate holder and the secondary chamber. The connecting passage is adapted to be covered by the substrate when the substrate is mounted on the front surface of the substrate holder. A passive low pressure source is fluidly connected to the secondary chamber.

According to further embodiments of the present invention, a pressure chamber assembly for use with a substrate includes a vessel and a substrate holder assembly. The vessel defines a pressure chamber. The substrate holder assembly includes a substrate holder disposed in the pressure chamber, the substrate holder including a front surface adapted to support the substrate, and a housing defining a secondary chamber. A restrictive passage provides fluid communication between the pressure chamber and the secondary chamber. At least one connecting passage provides fluid communication between the front surface of the substrate holder and the secondary chamber. The connecting passage is adapted to be covered by the substrate when the substrate is mounted on the front surface of the substrate holder. A low pressure source is fluidly connected to the secondary chamber.

According to method embodiments of the present invention, a method for holding a substrate to a substrate holder in a pressure chamber includes providing a first pressure in the pressure chamber. A substrate holder assembly is provided including a substrate holder disposed in the pressure chamber, the substrate holder including a front surface adapted to support the substrate, and a housing defining a secondary chamber. At least one connecting passage provides fluid communication between the front surface of the substrate holder and the secondary chamber. The substrate is mounted on the substrate holder such that the substrate covers the connecting passage. A second pressure is provided in the secondary chamber that is lower than the first pressure using a passive low pressure source.

According to further method embodiments of the present invention, a method for holding a substrate to a substrate holder in a pressure chamber includes providing a first pressure in the pressure chamber. A substrate holder assembly is provided including a substrate holder disposed in the pressure chamber, the substrate holder including a front surface adapted to support the substrate, and a housing defining a secondary chamber. A restrictive passage provides fluid communication between the pressure chamber and the secondary chamber. At least one connecting passage provides fluid communication between the front

surface of the substrate holder and the secondary chamber. The substrate is mounted on the substrate holder such that the substrate covers the connecting passage. A second pressure is provided in the secondary chamber that is lower than the first pressure.

According to embodiments of the present invention, a pressure chamber assembly for retaining a fluid includes first and second relatively separable casings defining an enclosed chamber and a fluid leak path extending from the chamber to an exterior region. An inner seal member is disposed along the leak path to restrict flow of fluid from the chamber to the exterior region. An outer seal member is disposed along the leak path between the inner seal member and the exterior region to restrict flow of fluid from the chamber to the exterior region. The inner seal member is a cup seal.

According to further embodiments of the present invention, a pressure chamber assembly for retaining a fluid includes first and second relatively separable casings defining an enclosed chamber and a fluid leak path extending from the chamber to an exterior region. An inner seal member is disposed along the leak path to restrict flow of fluid from the chamber to the exterior region. An outer seal member is disposed along the leak path between the inner seal member and the exterior region to restrict flow of fluid from the chamber to the exterior region. The inner seal member is a cup seal. The inner seal member is adapted to restrict flow of fluid from the chamber to the exterior region when a pressure in the chamber exceeds a pressure of the exterior region. The outer seal member is adapted to restrict flow of fluid from the exterior region to the chamber when a pressure in the chamber is less than a pressure of the exterior region.

According to embodiments of the present invention, a pressure chamber assembly for processing a substrate includes a pressure vessel defining an enclosed pressure chamber. A substrate holder is disposed in the pressure chamber and is adapted to hold the substrate. A drive assembly is operable to move the substrate holder. The drive assembly includes a first drive member connected to the substrate holder for movement therewith relative to the pressure vessel and a second drive member fluidly isolated from the first drive member and the pressure chamber. A drive unit is operable to move the second drive member. The drive unit is fluidly isolated from the first drive member and the pressure chamber. The

second drive member is non-mechanically coupled to the first drive member such that the drive unit can move the substrate holder via the first and second drive members.

According to further embodiments of the present invention, a pressure chamber assembly for processing a substrate includes a pressure vessel defining an enclosed pressure chamber. A substrate holder is disposed in the pressure chamber and is adapted to hold the substrate. A magnetic drive assembly is operable to move the substrate holder relative to the pressure vessel.

According to further embodiments of the present invention, a pressure chamber assembly for processing a substrate includes a pressure vessel defining an enclosed pressure chamber and an exterior opening in fluid communication with the pressure chamber. A substrate holder is disposed in the pressure chamber and is adapted to hold the substrate. A drive assembly is operable to move the substrate holder relative to the pressure vessel, the drive assembly including a housing covering the exterior opening of the pressure chamber so as to seal the exterior opening.

According to embodiments of the present invention, a pressure chamber assembly includes a pressure vessel and a guard heater assembly. The pressure vessel defines an enclosed chamber. The guard heater assembly includes a guard heater disposed in the chamber and interposed between a surrounding portion of the pressure vessel and a holding volume. The guard heater is adapted to control a temperature of the holding volume. The guard heater is insulated from the surrounding portion of the pressure vessel.

According to some embodiments of the present invention, the guard heater and the surrounding portion of the pressure vessel define an insulating gap therebetween. Preferably, the insulating gap has a width of at least 0.1 mm.

According to some embodiments of the present invention, the guard heater assembly includes a layer of insulating material disposed between the guard heater and the surrounding portion of the pressure vessel. Preferably, the layer of insulating material has a thickness of at least 0.1 mm.

The guard heater assembly may further include a second guard heater disposed in the chamber and interposed between a second surrounding portion of the pressure vessel and the holding volume. The second guard heater is adapted to

control the temperature of the holding volume. The second guard heater is insulated from the second surrounding portion of the pressure vessel.

A fluid spray bar may be mounted in the guard heater. A substrate holder may be disposed in the holding volume.

According to embodiments of the present invention, a process chamber assembly for use with a substrate and a flow of process fluid includes a vessel and a spray member. The vessel defines a chamber. The spray member includes at least one spray port formed therein adapted to distribute the flow of process fluid onto the substrate in the chamber. The spray member is operative to rotate about a rotational axis relative to the vessel responsive to a flow of the process fluid out of the spray member through the at least one spray port.

The spray member may include a distribution portion including a distribution channel therein, the at least one spray port extending from the distribution channel to exteriorly of the spray member.

The at least one spray port may extend at an angle with respect to the rotational axis. Preferably, the at least one spray port extends at an angle of between about 5 and 85 degrees with respect to the rotational axis.

The process chamber assembly may include a plurality of the spray ports formed in the spray member.

A bearing may be interposed between the spray member and the vessel to allow relative rotation between the spray member and the vessel.

According to further embodiments of the present invention, a spray member for distributing a flow of process fluid onto a substrate includes a spray member including at least one spray port formed therein adapted to distribute the flow of process fluid onto the substrate in the chamber. The spray member is operative to rotate about a rotational axis responsive to a flow of the process fluid out of the spray member through the at least one spray port.

The spray member may include a distribution channel therein, the at least one spray port extending from the distribution channel to exteriorly of the spray member.

The at least one spray port may extend at an angle with respect to the rotational axis. Preferably, the at least one spray port extends at an angle of between about 5 and 85 degrees with respect to the rotational axis.

The spray member may include a plurality of the spray ports formed in the spray member.

The spray member may include a bar-shaped distribution portion, the at least one spray port being formed in the distribution portion. Alternatively, the spray member may include a disk-shaped distribution portion, the at least one spray port being formed in the distribution portion.

According to method embodiments of the present invention, a method of applying a process fluid to a substrate includes placing the substrate in a chamber of a vessel. A spray member is provided including at least one spray port formed therein. The process fluid is distributed from the at least one spray port onto the substrate. The spray member is rotated about a rotational axis relative to the vessel by flowing the process fluid out of the spray member through the at least one spray port.

Objects of the present invention will be appreciated by those of ordinary skill in the art from a reading of the figures and the detailed description of the preferred embodiments that follow, such description being merely illustrative of the present invention.

Brief Description of the Drawings

Figure 1 is a block diagram of an apparatus according to embodiments of the present invention;

Figure 2 is a block diagram of a chemistry supply/conditioning system forming a part of the apparatus of **Figure 1**;

Figure 3 is a block diagram of an alternative chemistry supply/conditioning system forming a part of the apparatus of **Figure 1**;

Figure 4 is a block diagram of a further alternative chemistry supply/conditioning system forming a part of the apparatus of **Figure 1**;

Figure 5 is a block diagram of an alternative recirculation system forming a part of the apparatus of **Figure 1**;

Figure 6 is a block diagram of a further alternative recirculation system forming a part of the apparatus of **Figure 1**;

Figure 7 is a block diagram of a supply/recovery system according to embodiments of the present invention;

Figure 8 is a cross-sectional view of a pressure chamber assembly according to embodiments of the present invention in a closed position;

Figure 9 is a cross-sectional view of the pressure chamber assembly of **Figure 8** in an open position;

Figure 10 is a cross-sectional view of an upper guard heater forming a part of the pressure chamber assembly of **Figure 8**;

Figure 11 is a top plan view of the upper guard heater of **Figure 10**;

Figure 12 is a bottom plan view of the guard heater of **Figure 10**;

Figure 13 is a cross-sectional view of a lower guard heater forming a part of the pressure chamber assembly of **Figure 8**;

Figure 14 is a bottom plan view of the lower guard heater of **Figure 13**;

Figure 15 is an enlarged, cross-sectional, fragmentary view of the pressure chamber assembly of **Figure 8**;

Figure 16 is a perspective view of a cup seal forming a part of the pressure chamber assembly of **Figure 8**;

Figure 17 is a fragmentary, perspective view of the cup seal of **Figure 16**;

Figure 18 is a cross-sectional view of a pressure chamber assembly according to further embodiments of the present invention;

Figure 19 is a cross-sectional view of a pressure chamber assembly according to further embodiments of the present invention;

Figure 20 is a top plan view of a chuck forming a part of the pressure chamber assembly of **Figure 19**;

Figure 21 is a bottom plan view of the chuck of **Figure 20**;

Figure 22 is a cross-sectional view of the chuck of **Figure 20** taken along the line **22-22** in **Figure 21**;

Figure 23 is a cross-sectional, schematic view of a pressure chamber assembly according to further embodiments of the present invention;

Figure 24 is a top plan view of a chuck forming a part of the pressure chamber assembly of **Figure 23**;

Figure 25 is a cross-sectional view of the chuck of **Figure 24** taken along the line **25-25** of **Figure 24**;

Figure 26 is a cross-sectional view of a pressure chamber assembly according to further embodiments of the present invention;

Figure 27 is a bottom view of a spray member forming a part of the pressure chamber assembly of **Figure 26**;

Figure 28 is a cross-sectional view of the spray member of **Figure 27** taken along the line **28-28** of **Figure 27**; and

Figure 29 is a bottom plan view of a spray member according to further embodiments of the present invention.

Detailed Description of the Preferred Embodiments

The present invention now is described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

The present invention relates generally to, *inter alia*, the cleaning or treating of microelectronic substrates (such as semiconductor substrates) during or subsequent to the manufacturing of integrated circuits, microelectronic devices, MEM's, MEOM's and opto-electronic devices. Removal of surface contaminants and particulates is a key step in the integrated circuit fabrication process. There are numerous cleaning steps (commonly referred to as "cleans") in the fabrication process. The different types of cleans include pre-diffusion cleans, front end of the line post-ash cleans, back end of the line post-etch cleans, pre-metal deposition cleans, front end of the line plasma strip, back end of the line clean/strip, post-ion implantation cleans and post-chemical mechanical planarization (CMP) cleans. There are many types and sources of particulates and contaminants in the fabrication process. The particles and contaminants may be molecular, ionic, atomic or gaseous in nature. The source may be inherent (*e.g.*, redeposition of resist) or extrinsic to the process (*e.g.*, wafer transport).

The shift of interconnect systems shift from Al/SiO_2 to Cu/low-k presents new challenges that may be effectively addressed using the methods and apparatus of the present invention. For example, a primary problem with the transition to Cu is the tendency of Cu to corrode when exposed to an oxidizing environment,

because Cu does not have the self-passivating properties of Al. Corrosion of Cu during cleans of dual damascene structures can result in high contact resistance, undercutting and lift-off of the dielectric layers, thereby reducing circuit yields. Additional concerns have focused on the chemical compatibility of traditional cleans with low-k materials. As an example, it has been demonstrated that amine chemistries gas from OSG and other inorganic spin-on dielectric films, causes via poisoning. Aspects of the present invention may address the currently challenging cleans of these new interconnect systems.

With reference to **Figure 1**, an apparatus **10** according to preferred embodiments of the present invention is shown therein. As illustrated, the apparatus **10** is adapted to clean a surface of a wafer substrate **5**. However, it will be appreciated by those of skill in the art from the description herein that various features and aspects of the apparatus and the methods described hereinbelow may be used for cleaning or otherwise treating wafers or other types of substrates or workpieces. Additionally, it will be appreciated by those of skill in the art from the description herein that various components and steps as described herein below may be omitted or replaced with other (for example, conventional) components or steps as appropriate.

The wafer **5** may be, for example, a wafer of semiconductor material such as silicon, silicon oxide, gallium arsenide, etc. The wafer **5** has a substantially planar work surface **5A** and an opposing substantially planar backside surface **5B**. A continuous or discontinuous layer of waste material is disposed on the work surface **5A**. The waste layer may be a layer of photoresist, reactive ion etch residue, chemical mechanical polishing residue or post-ion implantation residue. The waste material in the aforementioned layers may include inorganic or organic contaminants such as polymers based on stryenic, acrylic, novolac, cyclic olefinic maleic anhydride resins; etch residue based on ions of fluorine, chlorine, bromine or iodine; and slurry residue containing silica or alumina abrasives with other common slurry additives such as oxidizers, buffers, stabilizers, surfactants, passivating agents, complexing agents, corrosion inhibitors or other agents. Other types of workpieces may be cleaned or otherwise treated using the apparatus including, for example, MEMS, MEOMS, opto-electronic devices, and 3-D micro/nano-structures.

The apparatus **10** includes generally a flow/pressure control system **100**, a recirculation system **200**, a supply/recovery system **300**, a pressure chamber assembly **400**, and a substrate handling system **500** (**Figure 8**). The pressure chamber assembly **400** includes a pressure chamber **410**. As discussed in greater detail below, the wafer **5** is held in the pressure chamber **410** for processing. The flow/pressure control system **100** conditions and applies a chemistry or chemistries (also referred to as adjuncts or modifiers), CO_2 (in the form of liquid, gas, and/or supercritical fluid ($ScCO_2$)), and/or a mixture of chemistries and CO_2 to the working surface **5A** of the wafer **5**. The substrate handling system **500** holds the wafer **5** and, optionally, moves the wafer **5** to facilitate uniform cleaning. The recirculation system **200** may be used to filter and return process fluid to the pressure chamber **410**. The supply/recovery system **300** supplies the process fluids and may be employed to clean post-process effluent and, optionally, return a portion thereof (typically, recovered CO_2) for further use in the apparatus **10**.

Turning to the flow/pressure control system **100** in greater detail, the system **100** includes a tank **T1** containing CO_2 at high pressure. The pressure of the CO_2 in the tank **T1** is preferably between about 400 psi and 4000 psi, depending on the process(es) to be executed using the apparatus **10**. The volume of the tank **T1** is preferably at least 5 times the volume of the pressure chamber **410**. A temperature control device may be operatively connected to the tank **T1**. The temperature control device may be, for example, a temperature sensor and a heating coil or probe or heat exchanger. The temperature of the CO_2 in the tank **T1** is preferably between about 0 °C and 90 °C, depending on the processes to be executed using the apparatus **10**. The CO_2 may be in liquid, gas or supercritical phase.

A plurality of outlet lines **L3**, **L4** and **L5** are fluidly connected to the tank **T1**. In the event that it may be desired to supply liquid CO_2 from the tank **T1**, the lines **L3**, **L4** and **L5** preferably draw from a lower portion of the tank **T1** (*e.g.*, via a lower outlet or a dip tube). The outlet lines **L3**, **L4** and **L5** fluidly connect the tank **T1** to a chemistry supply/conditioning system **120** (schematically illustrated in **Figure 1** and described in greater detail below), a feed line **L1**, and a feed line **L2**. Valves **V1**, **V2** and **V3** are provided to control flow in the lines **L3**, **L4** and **L5**, respectively.

A plurality of chemistry supplies **S1, S2, S3** are fluidly connected to the system **120**. Each supply **S1, S2, S3** may include a single chemistry or multiple compatible chemistries that are combined at or upstream of the respective supply **S1, S2, S3**. The supplies may include the respective chemistries disposed in suitable containers. Where feasible, the containers are preferably at atmospheric pressure to allow for convenient refilling.

The chemistries provided by the supplies **S1, S2, S3** may include, for example: water; oxidizers such as peroxides or permanganates; acids such as hydrofluoric, sulfuric, and nitric; bases such as secondary and tertiary amines; ammonium hydroxide; solvents such as organic carbonates, lactones, ketones, ethers, alcohols, sulfoxides, thiols, and alkanes; surfactants such as block copolymers or random copolymers composed of fluorinated segments and hydrophilic or lipophilic segments; surfactants with siloxane-based components and hydrophilic or lipophilic components; conventional ionic and non-ionic hydrocarbon-based surfactants; and salts such as ammonium fluoride and choline. Incompatible chemistries are chemistries which, when combined or exposed to one another, tend to react with one another in a manner that impedes the process and/or damages or unduly fouls the apparatus **10** or wafer **5**. Examples of incompatible chemistries include acids and bases.

Level sensors may be provided in each of the supplies **S1, S2, S3** to indicate that a refill is needed and/or to provide a metric of chemistry use in the process. Means such as a heating coil or jacket may be provided to control the temperatures of the supplies. A mixing device may be provided in each supply **S1, S2, S3**.

As discussed in more detail below, the system **120** is operable to provide one or more controlled volumes of chemistry (with or without CO_2), which volumes may be conditioned by the system **120**. The feed lines **L1** and **L2** are each fluidly connected to the system **120** to receive the volume or volumes of the chemistries. The feed line **L1** is fluidly connected to a nozzle **191** in fluid communication with the pressure chamber **410**. The feed line **L2** is fluidly connected to a spray member **190** in the pressure chamber **410**. Filters **F1** and **F2** are provided in the feed lines **L1** and **L2**, respectively. Preferably and as

illustrated, the filters **F1**, **F2** are located downstream of all lines that feed into the feed lines **L1**, **L2**.

A vacuum line **L16** is fluidly connected to the pressure chamber **410**. A vacuum unit **P1** is operable to draw a full or partial vacuum in the pressure chamber **410** through the line **L16**. The vacuum unit **P1** may be a pump or one or more tanks that are maintained at or near vacuum at all times by a continuously operating vacuum pump. A vacuum tank may be advantageous in that the pressure chamber **410** may be evacuated more rapidly and the tank may be re-evacuated while wafer processing is occurring. If multiple vacuum tanks are used, they may be staged in their operation to generate greater vacuum in the pressure chamber **410** in less time.

The vacuum unit **P1** may be advantageous for managing the air (or ambient gas) introduced to the system. In each batch step, the pressure chamber **410** may be opened and closed to insert and/or remove a substrate. During the time when the pressure chamber **410** is open, the chamber may fill with ambient gas (typically, air). Active control and management using the vacuum unit **P1** may be used to prevent this insertion of ambient gas from building up over time in the process fluids (assuming some level of recycling of the process fluids is accomplished).

A circulation line **L6** fluidly connects the pressure chamber **410** and the system **120**. Preferably, the line **L6** draws from a lower portion of the pressure chamber **410**.

A secondary gas supply tank **T2** is fluidly connected to the pressure chamber **410** with a controllable valve **V15** provided therebetween. Preferably, the secondary gas has a higher saturated vapor pressure than CO_2. Preferably, the secondary gas is an inert gas. More preferably, the secondary gas is helium, nitrogen or argon.

Pulsing feature

A variable volume device or pulse generator **102** may be fluidly connected to the pressure chamber **410**. The pulse generator **102** includes a chamber **102B** and a pressurizing member **102A** movable in the chamber **102B**. The pulse generator **102** is operable to generate a rapid decrease and/or increase (*i.e.*, pulse)

in pressure in the pressure chamber **410**. Preferably, the swept volume of the pressurizing member **102A** is between about 0.1 and 5 times the volume of the pressure chamber **410**. Preferably, the pulse generator **102** is adapted to provide pressure pulsing cycles at a rate of between about 1 cycle/10 seconds and 50 cycles/second. Preferably, the pulse generator **102** is adapted to decrease and/or increase the pressure in the pressure chamber **410** by at least 100 psi, and more preferably by between about 300 psi and 1500 psi.

The pulse mechanism may be any suitable mechanism including, for example, a piston coupled to a linear actuator, a rotating shaft and a connecting rod, a magnetic piston movable by means of an external electric coil, and/or an electrically, pneumatically or hydraulically driven piston or diaphragm. In a hydraulic or pneumatic system, the pulse mechanism may be paired with valving to quickly admit and release pressure to the non-process side of the diaphragm thereby displacing the piston or diaphragm. In one embodiment, the high pressure tank **T1** and a low pressure vessel such as **T2** may be fluidly connected to provide motive force for the pulse mechanism (piston or diaphragm).

Suitable valving (not shown) may be added such that the pulse chamber **102B** is filled from one pathway, a valve in this pathway may be closed and the fluid may thereafter be driven back to the pressure chamber **410** through a second pathway including a filter. The second pathway may feed the returning fluid to the pressure chamber **410** through the spray member **190**. The multiple pathways may serve to prevent the reintroduction of contaminants just removed from the wafer or particles generated in the pulse chamber, if a piston is used.

While the pulse generator **102** is illustrated as connected to a bottom portion the pressure chamber **410**, the pulse generator **102** may draw from any height of the pressure chamber **410**. In particular, it may be desirable to configure the pulse generator **102** to draw from an upper portion when used to facilitate processes utilizing two-phase (liquid/gas) process fluids in the pressure chamber **410** or to affect fluid and particulate flow in the vicinity of the wafer. It may be advantageous to move fluid rapidly away from the substrate surface (vertically), rather than move it across (parallel to) the wafer's surface as a bottom nozzle would. A relatively large pulse chamber may be used to enable particle dislodgement from the wafer surface and also enable particle transport well away

from the wafer, to prevent redeposition. A relatively large pulse chamber may also be used to enable phase changes through two phases – such as from supercritical to liquid to gas.

An outlet line **L10** and a valve **V6** are provided to selectively vent the pressure chamber **410** to a lower pressure region, such as to a low pressure tank **T2** as discussed below, a fluid transfer device (*e.g.*, a pump), or atmosphere. Waste effluent from the pressure chamber **410** may be drawn off to the low pressure region.

In addition to allowing removal of waste from the pressure chamber **410**, the line **L10** and the valve **V6** may be used in tandem with the high-pressure tank **T1** to generate pressure pulses in the pressure chamber **410**. This may be accomplished by raising the pressure in the pressure chamber **410** using the tank **T1** (*i.e.*, by controlling one or more of the valves **V1**, **V2**, **V3** and/or other valves to provide an open path between the tank **T1** and the pressure chamber **410**), closing the valve **V6**, and then rapidly dropping the pressure in the pressure chamber **410** by opening the valve **V6**. The waste effluent may go to a low pressure tank, for example, such as the tank **T2**. This sequence may be repeated as needed.

Chemistry Supply/Conditioning System

The chemistry supply/conditioning system **120** is operable to provide a selected flow or amount of chemical adjuncts from the supplies **S1**, **S2**, **S3** (more or fewer supplies may be used) to the pressure chamber **410**. Moreover, the system **120** may be operable to selectively control the pressure, temperatures and flow rates of chemistries or chemistry/CO_2. In accordance with the present invention, certain alternative configurations may be employed for the system **120** as described hereinbelow. It will be appreciated from the description herein that various aspects and features of the disclosed embodiments may be omitted or combined with or substituted for other aspects and features of the embodiments.

With reference to **Figure 2**, a chemistry supply/conditioning system **120A** is schematically illustrated along with certain relevant portions of the apparatus **10**. A fluid transfer device **P3** selectively draws or permits gravity flow of chemistry fluid ("first flow") from the supply **S1** to a reservoir **R1** at substantially ambient

pressure. A level measuring device **122** measures the volume of the fluid in the reservoir and thereby the volume of the chemistry to be delivered to the pressure chamber **410**. The fluid transfer device **P3** may also serve to determine the volume of the fluid in the reservoir **R1** by metering the flow through the device **P3**. The chemical adjunct in the reservoir may thereafter drain under force of gravity through a conditioning unit **C1** (as discussed below), the filter **F1**, and the line **L1** into the pressure chamber **410**.

Alternatively, CO_2 (*e.g.*, supercritical CO_2 ($ScCO_2$), liquid CO_2, or compressed liquid CO_2 or gaseous CO_2) from the tank **T1** may be delivered to the reservoir **R1** through a line **L3A** by operation of a valve **V1A**. A pressurized mixture of the adjunct and CO_2 is thereby delivered to the pressure chamber **410** through the unit **C1**, the filter **F1**, and the line **L1**.

With further reference to **Figure 2**, the system **120A** is adapted to deliver a second flow of chemistry-containing process fluid to the pressure chamber **410**, the second flow including chemistry from the supply **S2** which is not compatible with the supply **S1**. The system **120A** provides a flow path for the second flow that is separate from that used for the first flow. The second flow path includes elements **P4**, **R2**, **122**, and **C2** corresponding generally to elements **P3**, **R1**, **122**, and **C1**.

In the same manner as discussed above, the second flow may be a chemistry only stream (*i.e.*, no CO_2) that is transferred to reservoir **R2** via **P4** and then through the conditioning unit **C2**, the filter **F2**, and the line **L2** to the pressure chamber **410**. Alternatively, CO_2 from the tank **T1** may be introduced into the reservoir **R2** through a line **L3B** by operation of a valve **V1B** such that the adjunct/CO_2 is delivered to the pressure chamber **410** under pressure.

Figure 2 further illustrates the use of the circulation line **L6** to return process fluid from the pressure chamber **410** to the reservoir **R2** by using **P4** or a pressure differential. The returned fluid may be remixed with the second flow for reuse in the process. A further filter (not shown) may be provided in the line **L6**.

With reference to **Figure 3**, a chemistry supply/conditioning system **120B** according to further embodiments of the present invention is shown therein. The system **120B** is particularly well-suited for delivering gaseous chemistries. The system **120B** corresponds to the system **120A** except that the reservoirs **R1**, **R2** are omitted and high pressure CO_2 is made directly available to the conditioning units

C1, C2 via lines L3A, L3B and valves V1A and V1B. By operation of the fluid transfer device P3 (or P4), the system 120B may inject the adjunct S1 (or S2) through the conditioning unit C1 (or C2) and the filter F1 (or F2) and into the pressure chamber 410. Alternatively, high pressure CO_2 may be added to and mixed with the chemistry S1 or S2 in the respective conditioning unit C1, C2. In this case, the volume of the chemistry delivered to the pressure chamber 410 may be measured by metering the flow of the chemistry through the fluid transfer device P3 (or P4) or by measuring the volume change in the supply vessels S1 or S2. The flow rate(s) of chemistries and/or CO_2 to the conditioning units C1 and C2 may also be controlled to achieve a desired ratio of CO_2 to chemistry in the stream being delivered to chamber 410.

With reference to **Figure 4**, a chemistry supply/conditioning system 120C according to further embodiments of the present invention is shown therein. The system 120C includes a fluid transfer device P5 operable to selectively draw alternatingly from each of the supplies S1 and S2 as well as the supply of high pressure CO_2 from the tank T1 (via line L3A and valve V1A). The device P5 forces the selected chemistry through a conditioning unit C3 and one or both of the filters F1 and F2 (depending on the operation of valves V9 and V10) so that the fluid is ultimately injected into the pressure chamber 410 under pressure. Optionally, CO_2 from the tank T1 may be added to the selected chemistry by introducing the CO_2 into the conditioning unit C3 using the line L3B and the valve V1B. In order to prevent mixing of the incompatible chemistries S1, S2, CO_2 (preferably, pure $ScCO_2$) from the tank T1 is introduced through the line L3A to flush the fluid transfer device P5 and the remainder of the flow path to the pressure chamber 410 shared by the two chemistry flows.

Recirculation System

The recirculation system 200 includes an outlet line L7 fluidly connected to a lower portion of the pressure chamber 410. Lines L8 and L9 are in turn fluidly connected to the line L7 and also to the feed lines L1 and L2, respectively, upstream of the filters F1 and F2. A fluid transfer device P2 is operable to draw fluid from the pressure chamber 410 and force the fluid through the lines L8 and L9 and ultimately back into the pressure chamber 410. The recirculated fluid flow

may be combined with other fluid flow in the lines **L1** and **L2** (*e.g.*, from the system **120** and/or from the lines **L3** or **L4**). Valves **V4** and **V5** are provided in the lines **L8** and **L9**.

The recirculation system **200** may serve to provide additional fluid mechanical action to the wafer surface without requiring additional removal of CO_2 and/or chemistry and introduction of new CO_2 and/or chemistry. Moreover, the recirculation system **200** may serve to continuously clean (*e.g.*, filter, distill, or separate components through density modulation) the process fluid during the cleaning process.

An alternative recirculation system **200A** according to the present invention is shown in **Figure 5**. The system **200A** includes an outlet line **L14**. Return lines **L15** and **L16** fluidly connect the line **L14** to a recirculation nozzle **193** and the spray member **190**, respectively, in the pressure chamber **410**. A fluid transfer device **P6** is operable to force fluid from the pressure chamber **410** through a filter **F3** and back into the pressure chamber **410** through the nozzle **193** and/or the spray member **190**. Valves **V7** and **V8** are provided to enable alternating delivery of fluid to the spray member or recirculation nozzle and to prevent unintended back flow through the nozzle **193**.

A further alternative recirculation system **200B** according to the present invention is shown in **Figure 6**. The system **200B** includes an outlet line **L30** fluidly connecting the pressure chamber **410** to a still **243** (having a heating element **245**) through a transfer system **242**. The transfer system **242** converts the waste stream from the pressure chamber **410** from its starting state (*e.g.*, liquid, compressed liquid, or supercritical fluid) to a liquid. Preferably, the transfer system **242** is also adapted to prevent backflow of fluids from the still **243** to the pressure chamber **410**. For this purpose, the transfer system **242** may include one or more shut-off valves and/or one-way/check valves.

If the waste stream from the pressure chamber **410** is a liquid, the transfer system **242** may not change the fluid or may merely change the temperature of the fluid (*e.g.*, using a heater or chiller). If the waste stream from the pressure chamber **410** is a compressed liquid, the transfer system may provide a pressure let down (*e.g.*, by means of a torturous path, an orifice, or control valve). The transfer system **242** may also include a temperature-altering element. If the waste stream

from the pressure chamber **410** is a supercritical fluid, there is preferably a pressure let-down as discussed above as well as a temperature-altering step. In this case, it may be necessary or desirable to cool the fluid to cross into the 2-phase Liquid/Gas region of the phase diagram.

Once in the liquid state, the fluid is boiled/distilled in the still **243** to separate the fluid into two components: a lighter component, which will be predominantly CO_2 gas, and a heavier component which will be predominantly adjunct chemistry and entrained contaminants. The heavier component may be conveyed (*e.g.*, by gravity) to a recycling/disposal system **244**.

The CO_2 gas (lighter) stream is directed to a heat exchanger **246** via a line **L31** where the CO_2 gas stream is converted (through manipulation of temperature and pressure) to the conditions of the processing fluid (*i.e.*, liquid, compressed liquid or supercritical fluid). If the fluid starting condition was liquid, the exchanger may include a heat transfer coil **247** connected to the heating device so as to transfer heat from the condensing fluid to the still **243**. The CO_2 may be additionally cleaned through filtration, adsorption, absorption, membrane separation, physical separation (*e.g.*, centrifugal force) or electrostatic separation. The conditioned CO_2 may then be provided back to additionally process the substrate or to process a subsequent substrate. Additional chemistries may be added to this incoming fluid (*e.g.*, at a mixing reservoir **248**).

The distilling recirculation system **200B** may be used to provide a continuous or intermittent flow of the process fluid through the pressure chamber **410**. The mass flow may serve to assist in the cleaning process by transporting particulates away from the wafer **5** (*e.g.*, to prevent redeposit on the wafer) and/or providing mechanical action (agitation) on the wafer surface. The mass flow may be filtered or otherwise conditioned. The mass flow may be fully driven by the addition of heat in the still **243** so that no pumps or other potentially particulate-generating mechanical devices are required. Multiple transfer systems **242**, stills **243**, heat exchangers **246** may be used to provide increased continuous flow.

Each of the recirculation systems **200**, **200A**, **200B** may be employed to provide mass flow through the chamber **410** without loss of process fluid mass from the process loop (except the relatively small quantities of adjuncts and particulates that are filtered or distilled out of the process fluid stream. Moreover,

each of the recirculation systems **200**, **200A** may be employed to provide mass flow through the chamber **410** without altering the chemical composition of the process fluid.

As depicted in **Figures 1-5**, the filters **F1**, **F2** as well as the filter **F3** are preferably adapted to provide filtration of at least particles in the range of 10 nm (as in nanometers) to 50 microns. Suitable filters may include sintered filters, bag-type filters, magnetic filters, electrostatic filters, and/or combinations thereof. Preferably, as in the illustrated embodiments, every fluid stream pathway into the pressure chamber **410** has a filter as its final element before the pressure chamber **410**. In particular, all valves and fluid transfer devices for delivering fluid to the pressure chamber **410** are disposed upstream of at least one filter.

The conditioning units **C1**, **C2**, **C3** may include means for mixing the chemistries of the adjunct or for mixing the adjunct and CO_2 (when present) to promote homogeneity and solvation of adjuncts. The conditioning units may also include means for controlling the temperature of the adjunct or adjunct/CO_2. Suitable mixing devices or processes include mechanical mixers and flow mixing. Temperature control may be achieved using probes, internal coils, elements, and/or an external jacket, for example. An electrical heater or a fluid heat exchanger may be used, for example.

The fluid transfer devices **P3**, **P4**, **P5** are preferably capable of accurately and consistently metering a flow of fluid. Suitable devices may include diaphragm pumps, syringe pumps, or piston pumps, for example.

While particular arrangements have been illustrated and described herein, it will be apparent to those of skill in the art that various modifications may be made in keeping with the present invention. For example, in the system **120A** (**Figure 2**), the circulation line **L6** may feed to the fluid transfer device **P3** such that the flow from the line **L6** is directed to the line **L1**. Valving (not shown) may be provided to allow selection of the feed line (*i.e.*, **L1** or **L2**) for each flow path, so that the chemistry (with or without CO_2) from the supply **S1**, for example, can be directed to either or both of the spray member **190** and the nozzle **191**, as desired. The apparatus **10** may include one or more chemistry supply paths that include an in-line reservoir (*i.e.*, as in the system **120A**) and/or one or more parallel chemistry supply paths that are direct injection (*i.e.*, as in the system **120B**) and/or one or

more parallel chemistry supply paths that serve alternative supplies (*i.e.*, as in the system **120C**). Additional filters, fluid transfer devices, reservoirs, conditioning units and valving may be provided as needed to provide additional flexibility.

Cleaning/Pulsing Process

The apparatus **10** may be used to execute a wide range of processes wherein the wafer **5** in the pressure chamber **410** is subjected to fluid streams, pools and atmospheres, including chemical adjuncts, CO_2 and mixtures thereof, in various states (*e.g.*, liquid, gas, supercritical fluid). Such processes may serve to clean or otherwise treat (*e.g.*, coat) the wafer surface **5A**. For example, the apparatus **10** may be used to conduct methods as disclosed in the following commonly owned U.S. Patent Applications, the disclosures of which are hereby incorporated herein by reference in their entireties:

1. U.S. Patent Application Serial No. _____; inventors James P. DeYoung, James B. McClain, Michael E. Cole, and David E. Brainard; filed September 13, 2001; and titled *Methods for Cleaning Microelectronic Structures with Cyclical Phase Modulation* (Attorney Docket No. 5697-45IP);
2. U.S. Patent Application Serial No. _____; inventors James P. DeYoung, James B. McClain, Stephen M. Gross, and Joseph M. DeSimone; filed September 13, 2001; and titled *Methods for Cleaning Microelectronic Structures with Aqueous Carbon Dioxide Systems* (Attorney Docket No. 5697-45IP2);
3. U.S. Patent Application Serial No. _____; inventors James P. DeYoung, James B. McClain, and Stephen M. Gross; filed September 13, 2001; and titled *Methods for Removing Particles from Microelectronic Structures* (Attorney Docket No. 45IP3);
4. U.S. Patent Application Serial No. _____; inventor(s) James P. DeYoung, James B. McClain, and Stephen M. Gross; filed September 13, 2001; and titled *Methods for the Control of Contaminants Following Carbon Dioxide Cleaning of Microelectronic Structures* (Attorney Docket No. 5697-45IP4);

The following are exemplary processes that may be practiced in accordance with the present invention. Preferably, the valving, fluid transfer devices, and sensors are operatively connected to a computerized controller to provide feedback and control as needed to conduct the desired process steps.

The wafer **5** is inserted into the pressure chamber **410** and secured to the chuck **510** by any suitable means such as adhesive or clamps. More preferably, the wafer **5** is secured to the chuck in one of the manners described below with regard to the wafer holding assemblies **520** (**Figure 19**) and **550** (**Figure 23**). The door of the pressure chamber is thereafter closed and sealed.

Air and any other gases in the pressure chamber **410** are evacuated from the pressure chamber **410** through the line **L16** using the vacuum unit **P1**.

Optionally, chemistry from one or more of the supplies **S1**, **S2**, **S3** may be applied to the wafer using the chemistry supply/conditioning system **120** prior to pressurizing the pressure chamber **410**.

The pressure chamber **410** is thereafter pressurized with CO_2 (preferably liquid CO_2 or $ScCO_2$) from the high-pressure tank **T1**. Preferably, the pressure chamber **410** is pressurized to a pressure of at least 400 psi; and more preferably, between about 800 psi and 3000 psi. Additionally, the atmosphere in the pressure chamber **410** is maintained at a selected temperature (preferably between about 10°C and 80°C), for example, using a guard heater as discussed below.

Once the pressure chamber **410** is pressurized to the selected pressure, dense-phase CO_2 is circulated through the line **L2** to the spray member **190** and/or the nozzle **191**. The spray member directs the dense-phase CO_2 onto the wafer surface **5A**. Optionally, chemistry, with or without liquid or supercritical CO_2 mixed therewith, from one or more of the supplies **S1**, **S2**, **S3** may be applied to the wafer using the chemistry supply/conditioning system **120**.

The pulse generator **102** and/or the high-pressure tank **T1** and the valve **V6** are then used to effectuate cyclical phase modulation (CPM). More particularly, the pulse generator **102** and/or the high-pressure tank **T1** and the valve **V6** are operated (with appropriate temperature control of the process fluid) to effect phase changes between liquid, supercritical, and gas states. Preferably, the phase changes are effected between supercritical and liquid states in a cyclical fashion. For example, CPM processes as disclosed in the commonly owned U.S. Patent

Application Serial No. _____; inventors James P. DeYoung, James B. McClain, Michael E. Cole, and David E. Brainard; filed September 13, 2001; and titled *Methods for Cleaning Microelectronic Structures with Cyclical Phase Modulation* (Attorney Docket No. 5697-45IP), the disclosure of which is hereby incorporated herein by reference in its entirety, may be conducted.

During the CPM cycles, CO_2 or CO_2 with chemistry may be applied to the wafer **5** via the spray member **190**. Fluid and particulate matter from the pressure chamber **410** may be removed from the pressure chamber **410** and recirculated locally via the recirculation system **200** or **200A** and/or recirculated via the line **L6** and the system **120**.

The process fluid (dense-phase CO_2, adjuncts and waste matter) is removed from the pressure chamber **410** via the line **L10**. As discussed below, CO_2 may be withdrawn from the pressure chamber **410** to a recovery tank. The process pathways (including the pressure chamber **410**) may be flushed one or more times with pure liquid or supercritical CO_2 from the tank **T1**.

The foregoing steps of optionally applying one or more of the chemistries **S1**, **S2**, **S3** to the wafer (with or without $ScCO_2$), conducting CPM and removing the process fluid may be repeated as needed. Following the final CPM cycle, the process fluid is removed and optionally a rinsing fluid (*e.g.*, a co-solvent or surfactant) is dispensed from the supplies **S1**, **S2**, **S3** onto the wafer **5** (preferably under pressure from the spray member **190**).

The pressure chamber **410** and the process pathways (including the recirculation pathway) are thereafter flushed with $ScCO_2$ from the tank **T1** to remove adjuncts and remaining residues. If no rinse fluid is used, a pure CO_2 (liquid or supercritical) fluid is used to remove adjuncts and remaining contaminants from the substrate. The flushing dense-phase CO_2 may be recirculated, but is finally removed via the line **L10**. A final rinse of the wafer **5** and the pressure chamber **410** is preferably conducted using pure liquid or supercritical CO_2.

Thereafter, the pressure chamber **410** is depressurized and the wafer **5** is removed.

Preferably, the apparatus **10** is operable to apply the process fluid from the spray member **190** onto the wafer surface at a pressure of at least 400 psi, and more

preferably between about 800 psi and 3000 psi. The process may include applying the process fluid to wafer using the spray member **190** with the spray member **190** rotating relative to the wafer. Either or both the spray member (*e.g.*, the spray member **190** or the spray member **602**) and the chuck (*e.g.*, the chuck **510**, **522**, or **552**) may be rotationally driven.

Moreover, a flow of process fluid may be provided across the wafer **5** by feeding the process fluid into the chamber **410** via a feed nozzle (*e.g.*, the nozzle **191**) and simultaneously removing process fluid through one or more of the outlet lines (*e.g.*, the line **L7**, the line **L10**, the line **L11**, and/or the line **L6**). Preferably, the apparatus **10** is operable to provide such a flow through the chamber **410** at a rate of at least 2 gpm.

As noted above, the process may include simultaneously pulsing the density of the CO_2 containing process fluid and spraying the process fluid onto the wafer **5**. Likewise, if the phase modulation is accomplished using the pulse generator **102**, a flow of the process fluid through the chamber **410** may be provided at the same time as the density modulation. The wafer **5** and/or the spray member **190** may be simultaneously rotated.

In each of the foregoing steps involving the application of chemistries, the chemistries may be any suitable chemistries. In particular, it is contemplated that the chemistries may include co-solvents, surfactants, reactants, chelants, and combinations thereof. Notably, the separate flow paths and/or flushing means of the chemistry supply system **120** may be used to safely and effectively add incompatible chemistries to the chamber **410**.

The apparatus may deliver process components in different states (*e.g.*, liquid, gas, supercritical) to the chamber **410** and may allow for components in different states to coexist in the chamber **410**. The apparatus may provide heated CO_2 gas (*e.g.*, from the tank **T1**) to drain or flush process components from the cleaning chamber for cleaning steps using liquid CO_2. Alternatively, the apparatus may deliver a secondary gas such as helium, nitrogen or argon from the secondary gas tank **T3** to displace process fluids during a cleaning step and preceding a rinse step when either liquid or supercritical CO_2 is used as the primary process fluid during the cleaning step. The apparatus may also provide heated $ScCO_2$ (*e.g.*, supercritical CO_2) at a temperature higher than that of the primary processing fluid

but at a density lower than that of the primary processing fluids used to displace processing fluids after a cleaning step, but prior to a rinse step for cleaning steps using $ScCO_2$.

Supply/recovery system

The supply/recovery system **300** is adapted to supply and/or recycle and re-supply CO_2 and/or chemistry to the cleaning process. As the process proceeds, some CO_2 will be lost. The process may include batch cycles where the pressure chamber **410** is pressurized and depressurized many times in succession as the substrates (*e.g.*, wafers are moved through the CO_2-based processing equipment). For example, some CO_2 will be lost to atmosphere when the pressure chamber is opened to remove and replace wafers. Some CO_2 will be lost from the system in the waste stream that is drained from the system. Substantial amounts of the CO_2 will be contaminated or otherwise rendered unsuitable or potentially unsuitable for further recirculation through the process loop. For these reasons, it is necessary to provide sources of additional CO_2 to replenish the CO_2 lost from the process. Additionally, it may be desirable to recycle CO_2 as well as chemistry for reuse in the apparatus **10** or elsewhere.

Stock CO2 supply

With reference to **Figure 7**, the supply/recovery system **300** includes a CO_2 stock supply **312**. The supply **312** may be, for example, CO_2 supplied in one or more liquid cylinders, carboys of sub-ambient liquid, or bulk supply systems of sub-ambient liquid. The storage method preferably allows for supply of either liquid or gaseous CO_2.

The supply **312** is fluidly connected to the process chamber **410** via a line **L17**, which is provided with a valve **V11** to control the flow into the pressure chamber **410**. Preferably, the system **300** is adapted such that the CO_2 from the supply can be delivered directly (*i.e.*, without aid of any fluid transfers devices, pressurizing tanks, or the like) into the pressure chamber **410** at a desired pressure (preferably between about 15 and 50 psig). The supply **312** may be from a gas or liquid source.

CO_2 as commonly distributed for industrial and commercial uses (*e.g.*, food processing such as carbonation of beverages and freeze-drying, pH control, or dry ice) is not sufficiently clean for processing of micro-electronic substrates. Commonly, such CO_2 supplies include contaminants such as organic materials, other gases, water and particulate matter. Accordingly, the system **300** may include a purification unit **D1** between the supply **312** and the pressure chamber **410**. The purification unit **D1** is operative to purify the CO_2 supply to the requisite ultra-high cleanliness and purity. In this manner, the purification unit **D1** enables the effective use of food grade or industrial grade CO_2, thereby allowing the use of existing supply chains and distribution chains for CO_2.

The purification unit **D1** may include one or more of the following means for filtering gas or liquid CO_2:

1. Distillation: The CO_2 may be drawn from a gaseous supply or a gaseous portion of the supply. Liquid CO_2 may be drawn, boiled, relocated to a collection volume and re-condensed;
2. Filtration;
3. Membrane separation (preferably paired with distillation); and
4. Absorption/adsorption (*e.g.*, capture based on attractive forces or molecule size).

CO_2 may also be delivered to the process (and, more particularly, to the pressure chamber **410**) by introducing additional CO_2 into the vapor-saver unit **320** discussed below. Preferably, this additional CO_2 is first purified using a purification unit corresponding to the purification unit **D1**.

Waste stream handling

As noted above in the discussion regarding the process, at various times (including, typically, at the end of each run), processing fluid may be removed from the pressure chamber **410** via the line **L10**. Such fluids may include liquid, gaseous, or supercritical CO_2, chemistry, and various contaminants (*e.g.*, particles dislodged from the wafer(s)).

The system **300** includes a low-pressure tank **T2** to receive the waste stream drawn removed from the pressure chamber **410**. The tank **T2** is preferably

maintained at a pressure of between about ambient and 3000 psi. The volume of the tank **T2** is preferably at least 5 times the volume of the pressure chamber **410**.

Different compositions may be expelled to the tank **T2**, in which case the tank **T2** is a segmented tank or multiple tanks. The pressure in the tank **T2** is less than that of a pressure head upstream of and fluidly communicating with the pressure chamber **410** so that the pressure differential forces the waste stream into the tank **T2** from the pressure chamber **410**. Preferably, the high-pressure tank **T1** provides the pressure head so that no pump or other mechanical device is required.

The reduction in pressure of the CO_2 as it is transferred from the pressure chamber **410** to the tank **T2** may be used to facilitate separation. Supercritical CO_2 process fluid may be expanded through a pressure reduction device (*e.g.*, a control valve or orifice) to a lower pressure. At this lower pressure, components of the processing fluid (*e.g.*, chemical adjuncts or entrained contaminants) may be rendered insoluble, thereby facilitating the efficient separation of the expanded stream into a light-fluid CO_2 stream and a heavy-fluid (insoluble) alternate stream.

A supercritical CO_2 process fluid may also be expanded through a pressure reduction to the two-phase Liquid/Gas area of the phase diagram. This may enable the segmentation of different process fluids in different segmented volumes of a divided tank or multiple tanks. Such segmentation may be advantageous to could mitigate the generation of mixed waste streams, which may be more costly to manage than single component fluid streams. Segmentation may also enable the utilization of distillation for separation of the processing fluid components (*e.g.*, separation of CO_2 for recycle from chemical adjuncts and entrained contaminants for disposal).

A liquid process fluid stream may be expanded and heated to the gas-state. This would allow a continuous distillation-like separation of components (*i.e.*, evaporation of flash evaporation), for example, as described below with regard the distillation system **340**.

Recycling and abatement

The waste stream received in the tank **T2** is thereafter transferred to a recycling/abatement station **310** through a line **L29** (which is provided with a valve **V12**). The waste stream may be transferred by means of a pump or the like, but is

preferably transferred using a non-mechanical means such as pressure differential and/or gravity. To the extent the waste stream has been separated in the tank **T2**, there may be two of more separate lines delivering the respective separated streams for separate handling by the unit **310**. These streams may be treated and directed by the system **300** in the following manners:

1. CO_2 may be disposed of through controlled venting or draining via a line **L27** to a safe atmospheric discharge and/or collection for unrelated use;

2. CO_2 may be directly supplied to the pressure chamber **410** via a line **L22**. The CO_2 is preferably purified by means of a purification unit **D3**. The CO_2 as delivered to the pressure chamber **410** through the line **L22** may be at greater than atmospheric pressure, in which case it may be used to perform or augment the pressurization of the main processing chamber at the beginning of each cycle;

3. CO_2 may be directed to the purification unit **D1** through the line **L23** and thereafter into the pressure chamber **410**;

4. Gaseous CO_2 may be directed through a purification unit **D2**, through a liquefying unit **314** (which adjusts the pressure and chills the CO_2 gas), and supplied to the stock CO_2 supply **312** for further use in the manner described above;

5. CO_2 may be passed through a purification unit **D4** and re-pressurized and supplied to the high-pressure tank **T1** through a line **L25** using a pressurizing device (*e.g.*, a pump) **P8**;

6. CO_2 may be directed via a line **L26** through a purification unit D5 to a vapor saver tank **320** as discussed below; and

7. Chemical adjuncts and contaminants may be treated and/or disposed of/recycled through a line **L28** and in accordance with good chemical stewardship.

Vapor recovery

Following draining of the process fluid from the pressure chamber **410**, a pressurized CO_2 vapor will remain in the pressure chamber **410**. It is desirable and

often necessary to remove this vapor prior to opening the pressure chamber **410** to remove the substrate(s) (*e.g.*, wafer(s)).

One method for depressurizing the chamber is to vent the chamber using a controlled release. Alternatively, a compressor or pump may be used to draw down the pressure in the pressure chamber **410**.

The pressure of the CO_2 may also be reduced using a vapor recovery system **322** and method as follows. Such methods and apparatus may employ features and aspects of the methods and apparatus disclosed in U.S. Patent Application Ser. No. 09/404,957, filed September 24, 1999 and in U.S. Patent Application Ser. No. 09/669,154, filed September 25, 2000.

A vapor recovery tank or pressurized container **322** is used to rapidly capture CO_2 (typically, gas or SCF) at the end of a process cycle through a line **L18**. The captured CO_2 is typically a gas or supercritical fluid, but may be a liquid (in which case, the venting is preferably from the bottom of the chamber **410** to avoid formation of solid/dry ice). In this manner, the pressure chamber **410** may be depressurized very rapidly. Advantageously, the capturing method is not constrained by the volumetric throughput of a mechanical device (*e.g.*, a compressor). The volume of the vapor recovery tank **322** is preferably on the order of one to 500 times the volume of the pressure chamber **410**.

The captured CO_2 may be handled in any desired manner, including:

a) it may be disposed of through a line **L21** having a valve **V10**, and preferably through a surge tank **324**;

b) using the line **L21** and surge tank **324**, it may be recovered and recycled for use in another application (*e.g.*, a CO_2-based fire suppression system or a storage container for recycle for use in some other service);

c) it may be recovered and recycled for use in the same application (compressed and/or liquified, and/or converted into SCF) and re-supplied to the processing system or to the CO_2-supply system;

d) it may be used in the next processing step to pressurize the pressure chamber **410** (which may be a prerequisite for pressurizing the pressure chamber **410** up to sufficient pressure to effectively add CO_2-based processing fluids).

The vapor recovery system may include a compressor **P7** for assisting the transfer of material from the pressure chamber **410** to the vapor recovery tank(s). For example, at the end of a processing cycle, the pressure chamber **410** may be at high pressure (CO_2-gas at vapor pressure or a supercritical fluid, 300 < P (psia) < 3000) and the vapor recovery tank may be at a low pressure. In order to depressurize the pressure chamber **410** to a low (*e.g.*, ambient) pressure very quickly (*e.g.*, to allow opening of the chamber and removal of the substrate) while saving the majority of the CO_2, the two chambers may be equalized, and then:

a) a compressor may be used to push more CO_2 from the main processing chamber to the vapor-saver tank; and

b) a second vapor recovery tank may be used (*e.g.*, in cascading manner) to again rapidly equilibrate and additionally lower the pressure of the pressure chamber **410**.

A compressor may also be used to remove the material from the vapor recovery tank(s) between the end of a first run and the end of the next run at which time the vapor recovery tank(s) may be required to be at low pressure again. The captured CO_2 may be handled in any of the manners described above.

It will be appreciated that various valving and flow control apparatus in addition to that illustrated may be employed in the system **300**. The vapor-saver system **320** and the several options for handling the CO_2 from the waste stream of line **L10** are independent and any may be eliminated from the system **300** as desired. Each of the purification units **D2**, **D3**, **D4**, **D5** may correspond to the purification unit D1 (*i.e.*, may use any of the methods listed above - distillation, filtration, membrane separation, and absorption/adsorption). As an alternative to the several purification units **D2**, **D3**, **D4**, **D5**, two or more of these purification units may be combined so that the respective flow paths each have a common extent through the shared purification unit and thereafter diverge.

Pressure chamber assembly

With reference to **Figures 8** and **9**, the pressure chamber assembly **400** includes an upper casing **420** and a lower casing **430**. When in a closed position as shown in **Figure 8**, the casings **420**, **430** define a pressure chamber **410** therebetween and a sealing system **450** as described in more detail below seals the

chamber **410**. When in a closed position as shown in **Figure 8**, a pair of opposed clamps **440** surround end portions of the casings **420**, **430** to limit separation of the casings **420**, **430**. The clamps **440** can be displaced to allow the casings **420**, **430** to be separated into an open position as shown in **Figure 9**.

Guard heater

A guard heater assembly **460** is disposed in the chamber **410** and includes an upper guard heater **462** and a lower guard heater **472**. The guard heater assembly **460** defines a holding volume **411** between the heaters **462**, **472**. A platen or chuck **510** is disposed in the holding volume **411** between the guard heaters **462**, **472** and is adapted to support the wafer **5** for rotation about a vertical axis between the guard heaters **462**, **472**. A spray member **190** is mounted in a groove **464F** the upper guard heater **462** and adapted to direct fluid through nozzles **192** onto the working surface **5A** of the wafer.

The casings **420**, **430** are preferably each unitarily formed of stainless steel or other suitable metal. Passages **422A**, **422B**, **422C** are formed through the casing **420**. Passages **432A**, **432B**, **432C** are formed through the casing **430**. As best seen in **Figure 9**, the casing **420** has an annular flange **424** with an outer, annular recess **425** formed therein and defined in part by a vertical wall **425A**. The casing **430** has an annular flange **434** with an annular groove **435** formed therein. The flange **434** has a vertical wall **434A**. The casings **420** and **430** have opposing annular abutment faces **426** and **436**, respectively.

With reference to **Figures 10-12**, the upper guard heater **462** includes an interior member **464** having a top wall **464A** and an annular side wall **464B**. A spiral flow channel **466A** is formed in the top wall **464A**. An outer plate **467** covers the top wall **464A**. An annular surrounding member **468** surrounds the side wall **464B** and defines an annular surrounding channel **466B** therewith. A channel **466C** fluidly connects the channels **466A** and **466B**. An inlet **466D** in the top plate **467** fluidly connects the passage **422A** to the channel **466B**, and an outlet **466E** fluidly connects the passage **422B** to the channel **466A**. The outer plate **467** and the wall **468** are secured to the interior member **464** by welds **8**, for example. The spray member **190** extends through an opening **467A** in the outer plate **467** and is retained (*e.g.*, by an upstream nozzle or screws) in a groove **464C** in the top wall

464A. The nozzles **192** of the spray member **190** are fluidly connected to the passage **422C**. The interior member **464**, the outer plate **467** and the surrounding wall **468** are preferably formed of stainless steel. The guard heater **462** may be secured to the casing **420** by screws with small standoffs holding the screws off of the walls.

With reference to **Figures 13** and **14**, the lower guard heater **472** includes an interior member **478** and an outer plate **474** secured thereto by welds **8**, for example. An opening **479** extends through the outer plate **474**, and an opening **476D** extends through the interior member **478**. A spiral flow channel **476A** is formed in the interior member **478**. An inlet passage **476B** in the outer plate **474** fluidly connects the passage **432A** to the channel **476A**, and an outlet passage **476C** fluidly connects the passage **432B** to the flow channel **476A**. The interior member **478** and the outer plate **474** are preferably formed of stainless steel or other suitable metal. The guard heater **472** may be secured to the casing **430** by screws with small standoffs holding the screws off of the walls.

Preferably, the guard heaters **462**, **472** each have a surface area (*i.e.*, the "interior", inwardly facing surfaces) to volume ratio of at least 0.2 cm^2/cm^3. More preferably, the guard heaters **462**, **472** each have a surface area to volume ratio of between about 0.2 and 5.0 cm^2/cm^3, and most preferably of about 0.6 cm^2/cm^3.

As discussed above, the temperature of the wafer environment (*i.e.*, the chamber **410** and the fluid(s) therein) is preferably controlled during and between the cleaning and other process steps. The temperature in the chamber **410** is controlled using the guard heater assembly **460**. More particularly, a flow of temperature control fluid is introduced through the passage **422A**, through the inlet opening **466D**, through the channel **466B**, through the passage **466C**, through the passage **466A**, through the outlet opening **466E** and out through the passage **422B**. In this manner, heat from the temperature control fluid is transferred to the guard heater **462** to heat the guard heater **462** (when the fluid is hotter than the guard heater **462**) or, alternatively, heat from the guard heater **462** is absorbed and removed by the fluid to cool the guard heater **462** (when the fluid is cooler than the guard heater **462**). The lower guard heater **472** may be heated or cooled in the same manner by a temperature control fluid that flows through the passage **432A**,

through the inlet opening **476B**, through the channel **476A**, through the outlet opening **476C**, and through the passage **432B**.

The temperature control fluids may be any suitable fluid, preferably a liquid. Suitable fluids include water, ethelyne glycol, propelyne glycol, mixtures of water with either ethelyne or propelyne glycol, Dowtherm A (diphenyl oxide and diphenyl), Dowtherm E, (0-dichlorobenzene), mineral oil, Mobiltherm (aromatic mineral oil), Therminol FR (chlorinated biphenyl). Most preferably, the temperature control fluids are a 50%/50% mixture of water and ethelyne glycol. The fluid may be heated by any suitable means such as an electric, gas-fired or steam heater. The fluid may be cooled by any suitable means such as fluid chiller, for example, of vapor compression refrigeration type or evaporative type.

The guard heater assembly **460** and the casings **420**, **430** are spaced apart to define an insulating gap **470** therebetween that substantially envelopes the guard heaters **462**, **472**. More particularly, an insulating gap **470A** is defined between the outer plate **467** and the adjacent surrounding wall portions of the casing **420** and preferably has a width **A**. An insulating gap **470B** is defined between the surrounding wall **468** and the adjacent wall of the casing **420** and has a width **B**. An insulating gap **470C** is defined between the outer plate **474** and the adjacent surrounding wall portion of the casing **430** and has a width **C**. Preferably, each of the widths **A**, **B** and **C** is at least 0.1 mm. More preferably, each of the widths **A**, **B** and **C** is between about 0.1 and 10 mm, and most preferably about 1.0 mm.

The insulating gap **470** may serve to substantially increase the efficiency, controllability and manufacturing throughput of the system **10**. The insulating gap **470** may substantially thermally insulate the guard heaters **462**, **472** from the casings **420**, **430** so that the effect of the temperatures of the casings **420**, **430** on the atmosphere surrounding the wafer **5** is reduced or minimized. Restated, the insulation gap **470** may substantially limit the thermal mass that must be heated or cooled by the temperature control fluids to the thermal masses of the guard heaters **462**, **472**. Accordingly, the temperature of the process fluid may be controlled such that it is substantially different than that of the casings **420**, **430**.

While a fluid flow heating/cooling arrangement is illustrated and described above, other means for heating/cooling the guard heaters **462**, **472** may be employed in addition to or in place of fluid heating. For example, electrical

resistance coils (*e.g.*, designed to radiate heat directly to the wafer) may be provided in the guard heaters **462**, **472**.

With reference to **Figure 18**, a pressure chamber assembly **400A** according to alternative embodiments of the present invention is shown therein. The assembly **400A** differs from the assembly **400** only in that the guard heater assembly **460A** thereof includes insulating layers **471**, **473** in place of the insulating gap **470**. The guard heaters **462**, **472** may be secured to the insulating layers **471**, **473** which are in turn secured to the casings **420**, **430**, respectively.

The insulating layers **471**, **473** may be formed of crystalline fluoropolymers such as PCTFE (polychlorotrifluoroethylene), PTFE (polytetrafluoroethylene), or PVF2 (polyvinylidene difluoride). Preferably, the insulating layers **471**, **473** are formed of bulk PTFE, virgin PTFE or glass-filled PTFE. The insulating layers **471**, **473** may be honey-combed, open cellular, or otherwise constructed or configured to enhance the insulating performance thereof.

Preferably, the guard heater assemblies **460**, **460A** are adapted to provide temperatures in the pressure chamber **410** ranging from about 0 °C to 90 °C. Preferably, the guard heater assemblies **460**, **460A** are adapted to provide heat to the atmosphere in the pressure chamber **410** at a maximum rate of at least 500 joules/second.

Pressure chamber sealing system

The casings **420**, **430** which define the pressure chamber **410** also define a fluid leak path **3** (**Figure 15**) at the interface from the pressure chamber **410** to an exterior region **7** (*e.g.*, the ambient atmosphere (directly or indirectly)). The sealing system **450** is adapted to restrict (fully or partially) the flow of fluid along the fluid leak path **3**.

As best seen in **Figure 15**, the sealing system **450** includes an O-ring **452**, an annular cup (or chevron) seal **454**, an annular spring **456** and an annular retaining ring **458**. As discussed below, the combination of the seals **452**, **454** serves to improve the effectiveness and durability of the pressure chamber seal.

The retaining ring **458** is fixed to the flange **424** and extends radially outwardly toward the flange **434** and below the recess **425**. The retaining ring **458** may be formed of stainless steel or other suitable material. The retaining ring **458**

may be secured to the flange **424** by any suitable means, for example, threaded fasteners.

The cup seal **454** is shown in **Figures 16** and **17**. "Cup seal" as used herein means any self-energized seal that has a concave portion and is configured such that, when the concave portion of the seal is pressurized (*e.g.*, by a pressurized chamber on the concave side of the seal), the seal is thereby internally pressurized and caused to exert an outward force (*e.g.*, against adjacent surfaces of a pressure vessel defining the pressure chamber), to thereby form a seal. The cup seal **454** includes an annular inner wall **454B** joined along an annular fold **454C** to an annular outer wall **454A** and defining an annular channel **454D** therein.

The cup seal **454** is preferably unitarily formed of a flexible resilient material. Preferably, the cup seal **454** is formed of a material that is resistant to swelling and damage when exposed to dense CO_2. Suitable materials include fluorinated polymers and elastomers, such as PTFE (Teflon®, DuPont), filled PTFE, PTFE copolymers and analogs, such as FEP (fluorinated ethylene/propylene copolymers), Teflon AF, CTFE, other highly stable plastics, such as poly(ethylene), UHMWPE (ultra-high molecular weight poly(ethylene)), PP, PVC, acrylic polymers, amide polymers, and various elastomers, such as neoprene, Buna-N, and Epichlorohydrin-based elastomers. Suitable seal materials can be obtained from PSI Pressure Seals Inc., 310 Nutmeg Road South, South Windsor, CT 06074.

The cup seal **454** may be secured to the flange **424** by affixing at least one, and preferably both, of the inner wall **454B** and the fold **454C** to the adjacent portions of the flange **424** and/or the retaining ring **458**. The inner wall **454B**, **454C** may be secured to the flange **424** using adhesive, for example. Preferably, the cup seal **454** is retained by the retaining ring **458** without the use of adhesive or the like.

The spring **456** may be any suitable spring capable of repeatedly and reliably biasing the outer wall **454A** away from the inner wall **454B** (*i.e.*, radially outwardly). Preferably, the spring **456** biases the cup seal **454** radially outwardly beyond the flange **424** when the casings **420**, **430** are separated (see **Figure 9**). Preferably, the spring **456** is a wound wire spring or a cantilever type spring having a shape similar to, but smaller than, the cup seal **454** and nested inside the cup seal

454. The spring 456 is preferably formed of spring grade stainless steel. The spring 456 may be integrally formed with the cup seal 454. In addition to or in place of the provision of the spring 456, the cup seal 454 may be formed so as to have an inherent bias to spread the walls 454A, 454B apart. Moreover, the spring 456 may be omitted and the cup seal 454 may be provided with no inherent bias.

The O-ring 452 is disposed in the groove 435. Preferably, the O-ring 452 is secured in the groove 435 by an interference fit. The O-ring is formed of a deformable, resilient material. Preferably, the O-ring 452 is formed of an elastomeric material. More preferably, the O-ring 452 is formed of bunna-n or neoprene, and most preferably of EDPM. The O-ring 452 is sized such that, when the O-ring 452 is in its unloaded state (*i.e.*, when the casings 420, 430 are separated; see **Figure 9**), a portion of the O-ring 452 will extend above the abutment face 436.

When the casings 420, 430 are closed, the cup seal 454 is captured between the flanges 424 and 434 as shown in **Figures 8** and **15**. The spring 456 biases the walls 454A and 454B against the walls 434A and 425A, respectively. When the chamber 410 is pressurized above the ambient pressure, the pressure exerted in the channel 454D forces the walls 454A and 454B apart and into tighter, more sealing engagement with the respective walls 434A and 425A.

In this manner, the cup seal 454 provides a secure, primary seal that prevents or substantially reduces the flow of the fluid from the chamber 410 to the O-ring 452 along the fluid leak path 3. The O-ring 452 is thereby spared potentially damaging exposure to the process fluid. Such protection of the O-ring 452 may substantially extend the service life of the O-ring 452, particularly where the process fluid includes high pressure CO_2. Accordingly, the sealing system 450 may provide for a high throughput wafer manufacturing system with relatively long-lived seals.

Notably, when the chamber 410 is pressurized, the casings 420, 430 may be separated somewhat by the internal pressure so that the O-ring 452 is not well-loaded for sealing. Because the cup seal 454 serves as a primary seal, a secure sealing arrangement may nonetheless be provided. However, in the event of a partial or complete failure of the cup seal 454, the O-ring 452 may serve to prevent or reduce leakage of the process fluid to the environment. According to certain

embodiments, the assembly **400** may be adapted such that the O-ring **452** will allow fluid to pass along the fluid leak path **3** when the chamber **410** is at at least a selected pressure so that the O-ring is not pressurized and no damaging process fluid (*e.g.*, CO_2) is in contact with the O-ring for extended periods of time.

When the fluid in the chamber **410** is at atmospheric pressure or vacuum, the sealing effectiveness of the cup seal **454** will typically be diminished (however, the bias of the spring **456** may provide some sealing performance). In this event, the O-ring **452** may serve as the primary seal to prevent or reduce leakage of atmospheric fluid into the chamber **410** through the fluid leak path **3**. Notably, the atmospheric fluid (typically air) typically will not include high concentrations of CO_2 or other components unduly harmful to the O-ring material.

Preferably, and as illustrated, the O-ring **452** sealing arrangement is a butt-type arrangement so that no sliding components are present. The pressure energizing mechanism of the cup seal **454** allows for use of a relatively low bias force for the spring **456**. These aspects of the invention assist in minimizing the generation of any particles that may be detrimental to the wafer **5**. The cup seal **454** may be otherwise oriented or located in the pressure chamber assembly. Two or more of the cup seals **454** may be arranged in series along the fluid leak path.

From the description herein, it will be appreciated that the combination of a cup seal and an elastomeric O-ring seal overcomes certain problems associated with high pressure sealing of CO_2 holding vessels that typically neither an elastomeric O-ring seal nor a cup seal can overcome. In particular, elastomeric O-rings are generally not long-lived when exposed to high-pressure CO_2 and then rapidly depressurized. Cup seals when used as pressure seals typically require a large pre-load spring to enable the same vessel for vacuum service. Such large pre-load may cause greater friction and wear and, thus, generation of damaging/contaminating particles. In accordance with the present invention, the elastomeric O-ring may be externally energized (compressed) when required to establish a vacuum within the chamber.

Wafer holding assembly

With reference to **Figures 19-22**, a wafer holding assembly **520** according to further embodiments of the present invention is shown therein. The assembly

520 may be used in place of the chuck 510 in a pressure chamber assembly 400B (Figure 19) otherwise corresponding to the pressure chamber assembly 400. As will be better appreciated from the following description, the wafer holding assembly 520 includes a substrate holder or platen or chuck 522 and is adapted to retain the wafer on the chuck 522 by means of a pressure differential generated by rotation of the chuck 522.

The chuck 522 has a front surface 524 and an opposing rear surface 528. A plurality (as shown, eight) of impeller vanes 529 extend rearwardly from the rear surface 528 and radially outwardly with respect to a central rotation axis E-E (Figure 19). A plurality (as shown, four) of passages 526A extend fully through the chuck 522 from the rear surface 528 to a circumferential channel 526B formed in the front surface 524. A plurality (as shown, sixteen) of channels 526C extend radially outwardly from and fluidly communicate with the channel 526B. Additional circumferential channels (not shown) may fluidly connect the channels 526C.

As shown in Figure 19, the chuck 522 is mounted on a driven shaft 530 for rotation therewith about the rotational axis E-E. As the chuck 522 is rotated, the impeller vanes 529 tend to push or force the fluid between the rear surface 528 and the adjacent, opposing surface 412 of the pressure chamber 410 radially outwardly in the directions F toward the outer periphery of the chuck 522. A pressure differential is thereby generated beneath the chuck 522 between the inner region (*i.e.*, nearest the axis E-E) of the chuck 522 and the outer region of the chuck. More particularly, the pressure in the central region (including the pressure at the lower openings of the passages 526A) is less than the pressure at the outer edges of the chuck 522 and the pressure in the chamber 410 on the side of the wafer 5 opposite the chuck 522. As a result, a differential is created between the fluid pressure exerted on the top surface of the wafer 5 and the pressure of the fluid in the channels 526B, 526C.

In the foregoing manner, the wafer 5 is secured to the chuck 522 as the chuck 522 and the wafer 5 are rotated. In order to retain the wafer 5 on the chuck 522 prior to initiating rotation or during process steps without rotation, and/or in order to provide additional securement, supplemental holding means may be provided. Such supplemental means may include, for example, adhesive, clamps,

and/or an externally generated pressure differential assembly such as the wafer holding assembly **550** described below.

With reference to **Figures 23-25**, a wafer holding system **551** according to further embodiments of the present invention is shown therein. The system **551** includes a wafer holding assembly **550** and may be used in place of the chuck **510** in a pressure chamber assembly **400C** (**Figure 23**) otherwise corresponding to the pressure chamber assembly **400** (for clarity, certain elements of the assembly **400C** are not shown). The assembly **400C** is further provided with a magnetic drive assembly **580**.

As will be better appreciated from the following description, the wafer holding assembly **550** includes a substrate holder or platen or chuck **552** and is adapted to retain the wafer **5** on the chuck **552** by means of a pressure differential between the pressure in the pressure chamber **410** and the pressure at an outlet **564**. The magnetic drive system **580** is adapted to drive the chuck **552** relative to the pressure chamber **410** without requiring sealing directly between relatively moving elements (namely, a shaft **560** and the casing **430**). It will be appreciated that the wafer holding system **551** may be used with other drive arrangements and that the magnetic drive assembly **580** may be used with other wafer holder mechanisms.

Turning to the magnetic drive assembly **580** in greater detail, the assembly **580** includes an upper housing **585** and a lower housing **584**. The upper end of the upper housing **585** is received in the casing **430** such that a gas-tight seal is provided therebetween (*e.g.*, by means of a suitable sealing device such as a gasket). The shaft **560** extends through the housing **585** and is rotatably mounted thereon by upper and lower bearings **586** and **588**. A seal **561** is positioned between the shaft **560** and the housing member **585**. The seal **561** is preferably a non-contact seal. More preferably, the seal **561** is a gap seal (more preferably, defining a gap **G** having a width of between about 0.001 and 0.002 inch) or a labyrinth seal. The seal **561** may also be a lip seal or a mechanical seal.

An internal magnet holder **590** is mounted on the lower end of the shaft **560** for rotation therewith and has an inner magnet **M1** mounted on an outer portion thereof. The internal magnet carrier **590** is disposed in the lower housing member **584**. A pressure cap **596** surrounds the internal magnet carrier **590** and forms a gas-tight seal (*e.g.*, by means of a suitable sealing device such as a gasket) with the

lower end of the lower housing member **584**. In this manner, the pressure cap **596** and the upper housing member **585** together form a gas-tight reservoir for fluids that may enter the upper housing member **585** from the pressure chamber **410**.

A drive unit **582** is mounted on the housing member **584**. The drive unit **582** may be any suitable drive device such as a hydraulically driven unit or, more preferably, an electrically driven unit. The drive unit **582** is operable to rotate a shaft **594** that extends into the housing member **584**. An external magnet holder **592** is mounted on the shaft **594** for rotation therewith. The external magnet holder **592** is disposed in the housing member **584**, but is mechanically and fluidly separated from the internal magnet holder **590** and the pressure chamber **410** by the pressure cap **596**. An external magnet **M2** is mounted on the external magnet holder **592** for rotation therewith.

The magnets **M1** and **M2** are relatively constructed, arranged and configured to such that they are magnetically coupled to one another. In this manner, the magnets **M1**, **M2** serve to indirectly mechanically couple the external magnet holder **592** and the internal magnet holder **590**, and thereby the shaft **594** and the shaft **560**. Thus, the chuck **522** may be rotated by operation of the drive unit **582**.

The magnetic drive assembly **580** may be any suitable drive assembly with suitable modifications as described herein. Suitable magnetic drive assemblies include the BMD 150, available from Büchi AG of Uster, Switzerland. Moreover, other types of non-mechanically coupling drive units may be used.

As best seen in **Figures 24** and **25**, the chuck **552** has a front surface **554**. A countersunk passage **556B** extends fully through the chuck **552**. A plurality of channels **526A** extend radially outwardly from and fluidly communicate with the passage **556B**. Additional circumferential channels (not shown) may fluidly connect the channels **526A**.

As shown in **Figure 23**, the chuck **552** is mounted on the driven shaft **560** by a nut **558** for rotation with the shaft **560** about a rotational axis **F-F**. The shaft **560** has an axially extending connecting passage **562** extending therethrough. The nut **558** has a central aperture that allows fluid communication between the passage **562** and the passage **556B**. A passage **563** extends radially through the shaft **560** and fluidly connects the passage **562** to the secondary chamber **565**

defined between the housing **585** and the shaft **560**. Preferably, the seal **561** is a non-contact seal (*e.g.*, a gap seal or a labyrinth seal) forming a restricted flow passage that provides fluid communication between the pressure chamber **410** and the secondary chamber **565**.

An outlet **564** in the housing member **585** fluidly connects the secondary chamber **565** with a line **L40**. A line **L41** having a valve **V30** fluidly connects a flow restrictor **566** and a storage tank **568** to the line **L40**. The flow restrictor **566** may be a throttling orifice or a suitable partial closure valve such as a needle valve adapted to provide a controlled limit on flow therethrough. A line **L42** having a valve **V31** fluidly connects a fluid transfer device **P20** (*e.g.*, a vacuum pump) to the line **L40**.

The system **551** may be used in the following manner to secure the wafer **5** to the chuck **552**. A pressure is provided in the storage tank **568** that is less than the pressure of the atmosphere in the pressure chamber **410** under typical process conditions. During processing, the valve **V30** is opened so that the secondary chamber **565** is placed in fluid communication with the storage tank **568** which serves as a passive low pressure source (*i.e.*, no pump, compressor or the like is employed to generate the pressure or vacuum). In this manner, the pressure in the chamber **565** (and, therefore, in the fluidly communicating channels **556A**) is less than the pressure in the pressure chamber **410**. A pressure differential is thereby generated between the upper surface of the wafer **5** and the backside of the wafer **5**, causing the wafer **5** to be drawn down onto the chuck **552** in the direction **D**.

The flow restrictor **566** serves to limit flow of fluid from the secondary chamber **565** to the storage tank **568**, thereby providing a controlled leak. The controlled leak serves to ensure a that sufficient differential pressure is provided across the wafer **5** to hold it in place without allowing undue loss of the fluid from the pressure chamber **410**.

Preferably, the pressure of the storage tank **568** is greater than atmospheric pressure, but less than the pressure of the pressure chamber **410** during the intended processes. The storage tank **568** may permit gas that is drawn from the pressure chamber **410** to be cleaned and recycled or otherwise disposed of.

Alternatively, the storage tank **568** may be omitted or bypassed such that the line **L41** vents directly to atmosphere when the valve **V30** is opened.

If the pressure of the atmosphere in the pressure chamber **410** is the same as or less than the pressure of the passive low pressure source (*i.e.*, the storage tank **568** or the ambient atmosphere), the fluid transfer device **P20** may be operated to reduce the pressure in the chamber **565** to less than the pressure in the pressure chamber **410** to generate the desired amount of pressure differential across the wafer **5**. In this event, the valve **V30** is closed and the valve **V31** is opened.

Preferably, the system **551** is operable to generate a pressure in the channels **556A** that is at least 1 psi less than the pressure in the pressure chamber **410**, and more preferably, between about 5 and 20 psi less.

Rotating spray member

The spray member **190** as described above as well as the spray members **602, 652** described below provide dispersed inlets to deliver process fluids directly to the surface of the wafer. Moreover, the spray members provide a distributed stream of these fluids that incorporates mechanical action from the fluid/surface impingement. This mechanical action is generally the result of the momentum of the fluid stream coming out of the spray member.

Design of the spray member (including, for example, number, spacing and sizes of spray ports) may be used to selectively control the use of the energy transfer/mechanical action. Additionally, simultaneous rotation of the wafer may serve to generate shear (momentum) between the fluid and the wafer surface to further facilitate removal of materials from the surface.

With reference to **Figure 26**, a pressure chamber assembly **400D** according to further embodiments of the present invention is shown therein. The assembly **400D** may be the same as the assembly **400** (certain aspects not shown in **Figure 26** for clarity), for example, except for the provision of a rotating spray member assembly **600**. The assembly **400D** may include a rotatively driven wafer holder **510** or the wafer **5** may be held stationary. The spray member assembly **600** may be used with any of the above-described pressure chamber assemblies. Notably, the spray member assembly **600** may be used to provide relative rotation between a spray member and a wafer without requiring a rotating wafer holder.

The spray member assembly **600** includes a spray member **602** as also shown in **Figures 27** and **28**. The spray member **602** includes a shaft portion **610**

and bar-shaped distribution portion **620**. An axial passage **612** extends from an upper opening **614** and through the portion **610** and fluidly communicates with a lateral passage **622** in the portion **620**. A series of spray ports **624** extend from the passage **622** to the lower, outer edge of the distribution portion **620**. The spray member **602** may be formed of a highly oxidatively stable material such as **316** stainless steel.

A bearing **630** is fixed within a passage **427** in the casing **420** such that a flange **632** of the bearing **630** is received in an enlarged portion **427A** of the passage **427**. The bearing **630** is preferably a sleeve bearing as shown. The bearing **630** may be formed of PTFE, PE or PEEK. Preferably, the bearing **630** is formed of PTFE.

The shaft portion **612** extends through the bearing **630** and has a flange **616** overlying the flange **632**. An end cap **640** is securely mounted to the casing **420** in the portion **427A** and over the flange **616**, for example, by threading. Preferably, the end cap **640** forms a gas pressure tight seal with the casing **420**.

The end cap **640** is adapted to receive a supply of process fluid (*e.g.*, from a supply line **9**) such that the flow of process fluid is directed through a passage **642** and into the passage **612**. The fluid continues into the passage **622** and is dispensed through the ports **624**.

With reference to **Figures 27** and **28**, the ports **624** are angled with respect to the intended rotational axis **N-N** (see **Figure 28**) of the spray member **602**. Preferably, the ports **624** are disposed at an angle **M** (**Figure 28**) of between about 0 and 85, and more preferably of between about 30 and 60. The ports **624** are angled opposite the direction **R** (**Figure 27**) of intended rotation.

In use, the reaction force responsive the fluid exiting the ports **624** (*i.e.*, the hydraulic propulsion) causes the spray member **602** to rotate about the axis **N-N** within the bearing **630**. Notably, because the bearing **630** is mounted internally (*i.e.*, within the high pressure region) of the pressure chamber **410** separated from ambient pressure by the end cap **640**, the bearing is not subjected to loading from a substantial pressure drop thereacross.

Alternatively or in addition to the hydraulically driven rotation, the spray member **602** may be coupled to a drive unit. The spray member may be directly or indirectly mechanically coupled to the drive unit (*e.g.*, using a bearing/seal/drive

unit configuration) or may be non-mechanically coupled (*e.g.*, using a coupling force for electromagnetic or magnetic (permanent, electro- or induction-driven) coupling). Some or all of the ports **624** may be oriented parallel to the axis of rotation **N-N**.

A spray member **652** according to further embodiments of the present invention may be used in place of the spray member **602** and with any of the foregoing modifications or features. The spray member **652** has a shaft portion **660** and corresponds to the spray member **602** except that the bar-shaped distribution portion **620** is replaced with a plate- or disk-shaped distribution portion **670** having a pattern of spray ports **674** formed therein. The pattern of the spray ports **674** may be modified.

It will be appreciated that various of the inventions described hereinabove and as reflected in the claims that follow may be used for processes other than those specifically discussed above with regard to the preferred embodiments. For example, the means and methods for holding a wafer to a chuck may be employed to hold other types of substrates, in other types of processes (*e.g.*, processes not involving CO_2 or wafer fabrication). The supply/recovery system **300** and the subsystems thereof may be used in other systems and processes using CO_2-containing process fluids, such as chemical mechanical planarization (CMP) systems employing CO_2.

The foregoing is illustrative of the present invention and is not to be construed as limiting thereof. Although a few exemplary embodiments of this invention have been described, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention. Therefore, it is to be understood that the foregoing is illustrative of the present invention and is not to be construed as limited to the specific embodiments disclosed, and that modifications to the disclosed embodiments, as well as other embodiments, are intended to be included within the scope of the invention.

THAT WHICH IS CLAIMED IS:

1. A method for cleaning a microelectronic substrate, the method comprising:

a) placing the substrate in a pressure chamber;

b) circulating a process fluid including dense phase CO_2 through the chamber such that the process fluid contacts the substrate; and

c) cyclically modulating the phase of the CO_2 during at least a portion of the step of circulating the process fluid.

2. The method of Claim 1 wherein the step of circulating the process fluid includes introducing CO_2 into the chamber and removing CO_2 from the chamber during at least a portion of the step of cyclically modulating the phase of the CO_2.

3. The method of Claim 1 wherein the step of cyclically modulating the phase of the CO_2 includes changing the phase of the CO_2 from $ScCO_2$ to liquid CO_2 and thereafter from liquid CO_2 to $ScCO_2$.

4. The method of Claim 1 wherein the step of circulating the process fluid includes supplying CO_2 from a pressurized tank.

5. The method of Claim 4 wherein the step of circulating the process fluid further includes removing the process fluid from the chamber using a low pressure source.

6. The method of Claim 1 wherein the step of circulating the process fluid includes removing a portion of the process fluid from the chamber and re-introducing the portion of the process fluid into the chamber.

7. The method of Claim 6 including the step of filtering the portion of the process fluid between the steps of removing the portion of the process fluid and re-introducing the portion of the process fluid into the chamber.

8. The method of Claim 6 including the step of combining the portion of the process fluid with chemical adjuncts between the steps of removing the portion of the process fluid and re-introducing the portion of the process fluid into the chamber.

9. The method of Claim 1 wherein the step of cyclically modulating the phase of the CO_2 includes cycling a variable volume device.

10. The method of Claim 1 wherein the step of cyclically modulating the phase of the CO_2 includes alternating CO_2 mass flow between a supply of CO_2 and the chamber and between the chamber and a low pressure source, wherein the supply of CO_2 is at a higher pressure than the chamber and the low pressure source is at a lower pressure than the chamber.

11. The method of Claim 1 wherein the process fluid includes chemical adjuncts.

12. The method of Claim 1 including exposing the substrate to chemical adjuncts prior to exposing the substrate to dense phase CO_2.

13. The method of Claim 1 including introducing a composition comprising a stored chemical adjunct and stored dense phase CO_2 to the chamber concurrently.

14. The method of Claim 13 including filtering the composition prior to introducing the composition to the chamber.

15. The method of Claim 13 wherein the step of introducing the composition includes:

delivering the chemical adjunct to a reservoir;

delivering the CO_2 to the reservoir to form the composition; and

delivering the composition from the reservoir to the chamber at substantially ambient pressure.

16. The method of Claim 13 wherein the step of introducing the composition includes:

delivering the chemical adjunct to a conditioning unit;

delivering the CO_2 to the conditioning unit to form the composition; and

delivering the composition from the conditioning unit to the chamber at greater than ambient pressure.

17. The method of Claim 16 including, following the step of delivering the composition from the conditioning unit to the chamber:

delivering a second chemical adjunct to a second conditioning unit;

delivering CO_2 to the second conditioning unit to form a second composition; and

delivering the second composition from the second conditioning unit to the chamber at greater than ambient pressure.

18. The method of Claim 16 including, following the step of delivering the composition from the conditioning unit to the chamber:

flushing the composition from the conditioning unit with dense phase CO_2;

delivering a second chemical adjunct to the conditioning unit;

delivering CO_2 to the conditioning unit to form a second composition; and

delivering the second composition from the conditioning unit to the chamber at greater than ambient pressure.

19. The method of Claim 1 including draining the process fluid from the chamber following the steps of circulating the process fluid and cyclically modulating the phase of the CO_2.

20. The method of Claim 19 wherein the step of draining the process fluid includes displacing the process fluid using a pressurized gas having a higher saturated vapor pressure than CO_2.

21. The method of Claim 19 wherein the step of draining the process fluid includes:

introducing $ScCO_2$ to the into the chamber at a higher pressure and a lower density than the process fluid in the chamber; while simultaneously

removing the process fluid from the process chamber to a low pressure source having a lower pressure than the chamber.

22. The method of Claim 1 including rotating the substrate relative to the chamber during at least a portion of the step of cyclically modulating the phase of the CO_2.

23. A method for cleaning a microelectronic substrate, the method comprising:

a) placing the substrate in a pressure chamber;

b) spraying a process fluid including dense phase CO_2 onto the substrate in a chamber; and

c) cyclically modulating the phase of the CO_2 during at least a portion of the step of spraying the process fluid.

24. The method of Claim 23 wherein the step of spraying a process fluid includes spraying the process fluid from a spray member including a plurality of spray ports.

25. The method of Claim 24 including rotating the spray member relative to the substrate during the step of spraying a process fluid.

26. The method of Claim 23 including rotating the substrate relative to the spray member during the step of spraying a process fluid.

27. A method for cleaning a microelectronic substrate, the method comprising:

a) providing the substrate in a pressure chamber containing a process fluid including dense phase CO_2 such that the substrate is exposed to the CO_2; and

b) cyclically modulating the phase of the CO_2 by alternating CO_2 mass flow between a supply of CO_2 and the chamber and between the chamber and a low pressure source, wherein the supply of CO_2 is at a higher pressure than the chamber and the low pressure source is at a lower pressure than the chamber.

28. The method of Claim 27 wherein the step of cyclically modulating the phase of the CO_2 includes changing the phase of the CO_2 from $ScCO_2$ to liquid CO_2 and thereafter from liquid CO_2 to $ScCO_2$.

29. The method of Claim 27 including the steps of removing a portion of the process fluid from the chamber and re-introducing the portion of the process fluid into the chamber.

30. A method for cleaning a microelectronic substrate, the method comprising:

a) placing the substrate in a pressure chamber;

b) introducing a process fluid including dense phase CO_2 into the chamber such that the process fluid contacts the substrate to thereby clean the substrate;

c) removing a portion of the process fluid from the chamber; and

d) re-introducing the portion of the process fluid into the chamber.

31. The method of Claim 30 including the step of filtering the portion of the process fluid between the steps of removing the portion of the process fluid and re-introducing the portion of the process fluid into the chamber.

32. The method of Claim 30 including the step of purifying the portion of the process fluid between the steps of removing the portion of the process fluid and re-introducing the portion of the process fluid into the chamber to remove contaminants from the CO_2.

33. The method of Claim 30 including the step of combining the portion of the process fluid with chemical adjuncts between the steps of removing the portion of the process fluid and re-introducing the portion of the process fluid into the chamber.

34. A method for cleaning a microelectronic substrate, the method comprising:

a) placing the substrate in a pressure chamber;

b) introducing a process fluid including dense phase CO_2 into the chamber such that the process fluid contacts the substrate to thereby clean the substrate;

c) removing a portion of the process fluid from the chamber; and

d) distilling the portion of the process fluid removed from the chamber to separate CO_2 from other components of the process fluid; and

e) re-introducing the separated CO_2 into the chamber.

35. The method of Claim 34 including re-conditioning the separated CO_2 to substantially the same conditions as those of CO_2 in the chamber prior to the step of re-introducing the separated CO_2 into the chamber.

36. The method of Claim 34 wherein the dense phase CO_2 is $ScCO_2$.

37. The method of Claim 34 wherein the dense phase CO_2 is liquid CO_2.

38. A method for cleaning a microelectronic substrate, the method comprising:

a) cleaning a substrate in a process chamber using a process fluid including CO_2;

b) removing the used process fluid from the process chamber;

c) separating CO_2 from the used process fluid; and

d) reusing the separated CO_2 in the process chamber or a further process chamber.

39. The method of Claim 38 wherein the step of reusing the separated CO_2 includes reusing the separated CO_2 to clean the same substrate.

40 The method of Claim 38 wherein the step of reusing the separated CO_2 includes reusing the separated CO_2 to clean a second substrate.

41. The method of Claim 38 wherein the step of reusing the separated CO_2 includes reusing the separated CO_2 in a subsequent processing step.

42. An apparatus for cleaning a microelectronic substrate, the apparatus comprising:

a) a pressure chamber;

b) means for circulating a process fluid including dense phase CO_2 through the chamber such that the process fluid contacts the substrate; and

c) means for modulating the phase of the CO_2 while the process fluid is being circulated.

43. The method of Claim 42 including a pressurized tank adapted to deliver a supply of CO_2 to the chamber.

44. The apparatus of Claim 42 including a low pressure source adapted to facilitate removal of the process fluid from the chamber.

45. The apparatus of Claim 42 including a fluid transfer device operative to remove a portion of the process fluid from the chamber and to re-introduce the portion of the process fluid into the chamber.

46. The apparatus of Claim 42 wherein the means for modulating the phase of the CO_2 includes a variable volume device.

47. The apparatus of Claim 42 wherein the means for modulating the phase of the CO_2 includes a supply of CO_2 fluidly connectable to the chamber and a low pressure source fluidly connectable to the chamber, wherein the supply of CO_2 is at a higher pressure than the chamber and the low pressure source is at a lower pressure than the chamber.

48. The apparatus of Claim 42 including:

a supply of chemical adjunct;

a reservoir in fluid communication with the supply of chemical adjunct and the chamber; and

a supply of CO_2 in fluid communication with the reservoir;

wherein the reservoir is at substantially ambient pressure.

49. The apparatus of Claim 42 including:

a supply of chemical adjunct;

a conditioning unit in fluid communication with the supply of chemical adjunct and the chamber;

a supply of CO_2 in fluid communication with the conditioning unit; and

wherein the supply of CO_2 is at greater than ambient pressure.

50. The apparatus of Claim 49 including:

a supply of a second chemical adjunct; and

a second conditioning unit in fluid communication with the supply of second chemical adjunct and the chamber.

51. The apparatus of Claim 42 including a supply of a pressurized gas fluidly connected to the chamber, the supply of pressurized gas having a higher saturated vapor pressure than CO_2.

52. The apparatus of Claim 42 including a substrate holding assembly operable to rotate the substrate relative to the chamber.

53. An apparatus for cleaning a microelectronic substrate using a process fluid including dense phase CO_2, the apparatus comprising:

a) a pressure chamber;

b) a spray member operative to spray the process fluid onto the substrate in the chamber; and

c) means for cyclically modulating the phase of the CO_2.

54. The apparatus of Claim 53 wherein the spray member includes a plurality of spray ports.

55. The apparatus of Claim 54 including means for rotating the spray member relative to the substrate.

56. An apparatus for cleaning a microelectronic substrate, the apparatus comprising:

a) a pressure chamber containing a process fluid including dense phase CO_2; and

b) a supply of CO_2 fluidly connectable to the chamber, the supply of CO_2 being at a higher pressure than the chamber;

c) a low pressure source fluidly connectable to the chamber, the low pressure source being at a lower pressure than the chamber; and

d) fluid control devices operable to cyclically modulate the phase of the CO_2 in the chamber by alternating CO_2 mass flow between the supply of CO_2 and the chamber and between the chamber and the low pressure source.

57. An apparatus for cleaning a microelectronic substrate, the apparatus comprising:

a) a pressure chamber;

b) a supply of a process fluid including dense phase CO_2 fluidly connected to the chamber; and

c) a distilling system including a still fluidly connected to the chamber and operative to separate CO_2 from the process fluid, wherein the distilling system is operative to re-introduce the separated CO_2 into the chamber or a further chamber.

58. An apparatus for cleaning a microelectronic substrate, the apparatus comprising:

a) a process chamber containing a process fluid including CO_2;

b) means for removing used process fluid from the process chamber;

c) means for separating CO_2 from the used process fluid; and

d) means for returning the separated CO_2 to the process chamber or a further process chamber for subsequent use.